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# Combustion Syntheses of $CoAl_2O_4$ Powders Using Different Fuels

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**Abstract**

This research intends to analyse the potential use of $CoAl_2O_4$ as an opaque pigment for solar collector selective paints. The opacity of the pigment occurs when the average crystallite size is micrometric. The $CoAl_2O_4$ samples were synthesized through combustion methods using aspartic acid (Asp) or lysine (Lys) as fuels. The powders obtained were calcined at temperatures between 600°C and 1100°C. Afterwards, the product was characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR). It was observed a $CoAl_2O_4$ phase in all the samples. The lowest average crystallite size was ≈24nm corresponding to the sample obtained with Asp and calcined at 600°C, while both powders calcined at 1100°C showed sizes higher than 200nm. In the light of these results it is suggested the use of even higher calcination temperatures so as to obtain opaque pigments for solar collectors selective paints.



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*Keywords: combustion synthesis, $CoAl_2O_4$, selective painting, pigments.*

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## 1. Introduction

Cobalt aluminate ($CoAl_2O_4$) with a normal spinel structure has captured researcher attention as a ceramic pigment due to its technological significance (Cho and Kakihana, 1999). Its importance resides in that it is a pigment both thermally and chemically stable colored by an intense blue known as Thenard's blue. It resists acid and basic attacks; solar exposure and the action of other atmospheric agents. Consequently, it has been widely used for colorized plastics, paint, fibres, paper, rubber, glass, cement, and ceramic bodies (Salavati-Niasari et al., 2009).

The crystallite size of $CoAl_2O_4$ has a fundamental importance since it gives its particular properties to the material. Cobalt aluminate spinel in the form of a micron-sized pigment it is opaque whereas in the form of nano-sized pigment dispersed in a matrix, it evidences transparency together with color generation (Salavati-Niasari et al., 2009).

Recently, $CoAl_2O_4$ has been obtained by sol-gel (Salavati-Niasari et al., 2009-Chemlal et al., 2000), hydrolysis of mixed metal alkoxides (Otero et al., 1999), polymerized complex technique (Cho and Kakihana, 1999), and by an auto-ignited gel combustion process using citric acid as fuel (Li et al., 2003). The advantage of solution techniques is the synthesis of pure nanosized particles due to the quasiatomic dispersion of the component cations in liquid precursors at low temperatures (Cho and Kakihana, 1999). The present research introduces for the first time synthesis of $CoAl_2O_4$ using gel-combustion processes fueled by lysine (Lys) or aspartic acid (Asp). The product obtained was calcined at 600°C, 900°C and 1100°C and characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). The purpose of this research is to analyze the potential use of $CoAl_2O_4$ as an opaque pigment for solar collector selective paints. As mentioned before, the opacity occurs when the average crystallite size is micrometric.

## 2. Experimental procedure

$CoAl_2O_4$ samples were obtained by gel-combustion process using Lys ($C_6H_{14}N_2O_2$) or Asp ($C_4H_7NO_4$) as fuels, specially using a conventional stoichiometric route. All the chemical routes were performed using reagents of analytical grade. The final calcination temperatures were at 600°C, 900°C and 1100°C and lasted 2 hours.

### *2.1. Aspartic acid route*

The first solution was prepared dissolving 5g of $Co(NO_3)_2.6H_2O$ (Aldrich) and 1,43g of Asp (Aldrich) in distilled water to obtain an homogeneous solution. The Asp/Co molar ratio chosen was 28/45(0.62) calculated on the basis of the following stoichiometric combustion reaction:

$$45\ Co(NO_3)_2.6H_2O + 28\ C_4H_7NO_4 \rightarrow 15\ Co_3O_4 + 112\ N_2 + 368\ CO_2 + 59\ H_2O \quad (1)$$

The second solution was performed dissolving 5g of $Al(NO_3)_3 \cdot 9H_2O$ (Aldrich) and 1,77g of Asp in distilled water to obtain a homogeneous solution. The Asp/Al molar ratio chosen was 2/10(0.2) calculated on the basis of the following stoichiometric combustion reaction:

$$2\ Al(NO_3)_3 \cdot 9H_2O + 2\ C_4H_7NO_4 \rightarrow Al_2O_3 + 4\ N_2 + 8\ CO_2 + 25\ H_2O \quad (2)$$

The two solutions were mixed and formed the final precursor solution for the combustion process. The solution was thermally concentrated on a hot plate at 250°C until a viscous gel was obtained. Soon after, it ignited and the combustion process proceeded with flame. The obtained ashes were calcined, and the obtained powders were named according to their calcination temperatures as follows: $CoAl_2O_4$-Asp-600°C, $CoAl_2O_4$-Asp-900°C and $CoAl_2O_4$-Asp-1100°C.

*2.2. Lysine route*

This route is similar to the Asp route. Here, for the first solution, the Lys/Co relation chosen was 14/51(0.27) calculated on the basis of the following stoichiometric combustion reaction:

$$51\ Co(NO_3)_2.6H_2O + 14\ C_6H_{14}N_2O_2 \rightarrow 17\ Co_3O_4 + 65\ N_2 + 84\ CO_2 + 404\ H_2O \quad (3)$$

For the second solution the Lys/Al molar ratio chosen was 15/22(0.68) and calculated on the basis of the following stoichiometric combustion reaction:

$$22\ Al(NO_3)_3 \cdot 9H_2O + 15\ C_6H_{14}N_2O_2 \rightarrow 11\ Al_2O_3 + 96\ N_2 + 45\ CO_2 + 303\ H_2O \quad (4)$$

Obtained powders after combustion were named: $CoAl_2O_4$-Lys-600°C, $CoAl_2O_4$-Lys-900°C and $CoAl_2O_4$-Lys-1100°C.

*2.3. Materials characterization*

The phases present in the as-synthesized $CoAl_2O_4$ nanopowders (obtained after calcination) were identified by X-ray diffraction (XRD) using a Philips PW 3710 diffractometer operated with Cu-$K_\alpha$ radiation. Our data was compared with those reported in the Inorganic Crystal Structure Database (ICSD). The crystallite size was measured as from the width of Bragg peaks using Scherrer equation (Klug and L. Alexander, 1974). The morphology of the powders was analyzed by scanning electron microscopy (JEOL, model 6610 LV microscope) and transmission electron microscopy (TEM, JEOL 100 CX II microscope). The operation voltage was 100kV. In both cases, the preparation of samples was performed following conventional procedures. Fourier transform infrared spectra (FTIR) of powders were obtained by Bruker IFS 66 equipment.

## 3. Results and discussions

Fig. 1 shows XRD patterns of all the samples. All of them present the spinel (*Fd-3m*), face centered cubic crystal structure of $CoAl_2O_4$. The same structure is observed in $CoAl_2O_4$ powders synthesized by an auto-ignited gel combustion process using citric acid as fuel (Li et al., 2003).

Additionally, secondary peaks unidentified and of very low intensity at 35 and 41° are observed in the XRD pattern of $CoAl_2O_4$-Lys-600°C sample displayed in Fig. 2, while in the rest of the samples is exhibited only one peak at 35° this is seen in $CoAl_2O_4$-Asp-600°C sample also displayed in Fig. 2.

It has been observed a difference in the change of phases between the $Al_2O_3$ obtained by aspartic combustion process calcined at 600 to 1200°C (Gardey Merino et al., 2010) and the samples on this research where no change occurred. Consequently, the crystalline structure of the samples is the same ($CoAl_2O_4$) at different temperatures as expressed in Table 1. Moreover, a proportional increment in average crystallite size with the temperature was observed, without affecting the occurrence of the spinel phase. For example, it was determined a crystallite size of 54nm for $CoAl_2O_4$-Lys-600°C sample, and this measure was increased to 133nm for $CoAl_2O_4$-Lys-900°C and it was intensified up to 200nm for $CoAl_2O_4$-Lys-1100°C. The same phenomenon was observed in powders obtained with Asp where, at 600°C, it was observed the lowest crystallite size of 24nm. In relation to the influence of the type of fuel, it does not appear to determine consistently minor or mayor sizes on powders obtained but it will be necessary further experiments to prove it. In the light of the results, it is suggested the use of even higher calcination temperatures in order to obtain opaque pigments suitable for solar selective paints.

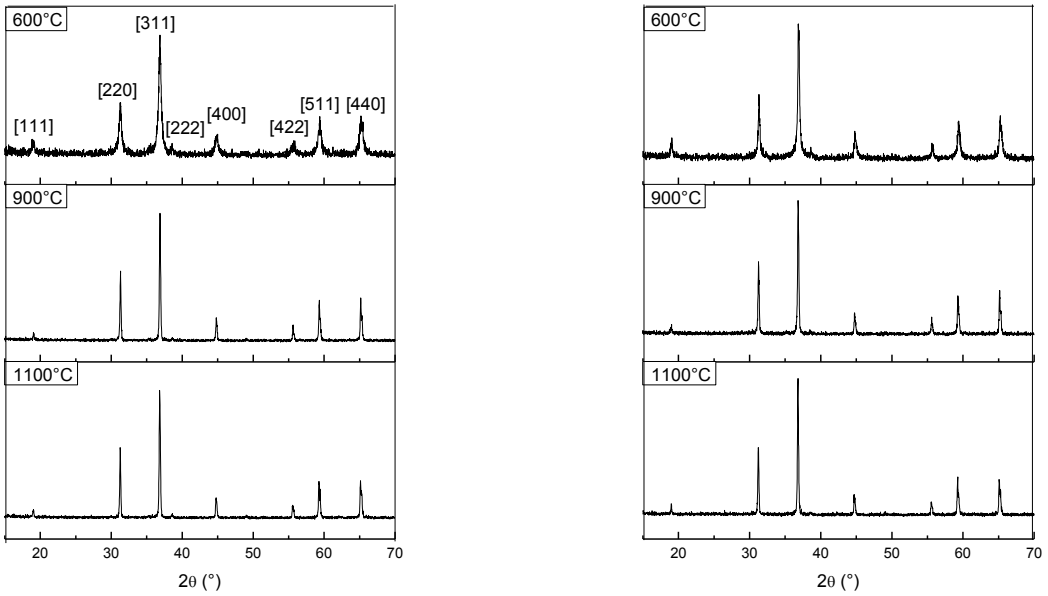


Fig. 1. XRD patterns of all obtained powders. The right side corresponding to those obtained with Asp route and the left with Lys route.

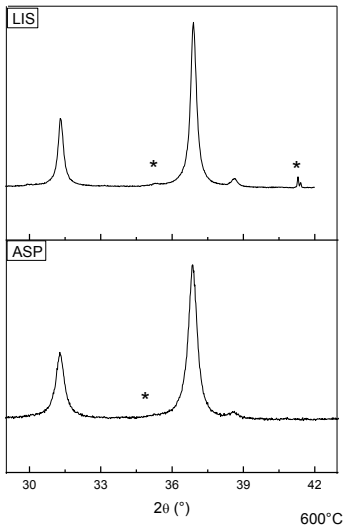


Fig. 2. XRD plots with selected angular range: Unidentified, low intensity secondary peaks, corresponding to $CoAl_2O_4$-Lis-600°C sample (up) and $CoAl_2O_4$-Asp-600°C sample (down).

Table 1. Crystalline phases and average crystallite size of obtained powders.

| Fuel | Calcination temperature (ºC) | Phase | Average crystallite size (nm) |
|---|---|---|---|
| Asp | 600 | $CoAl_2O_4$ | 24 ± 3 |
| Lys | 600 | $CoAl_2O_4$ | 54 ± 2 |
| Asp | 900 | $CoAl_2O_4$ | > 200 |
| Lys | 900 | $CoAl_2O_4$ | 133± 1 |
| Asp | 1100 | $CoAl_2O_4$ | > 200 |
| Lis | 1100 | $CoAl_2O_4$ | > 200 |

FT-IR spectrum was scanned for each sample, where all of them resulted identical. Fig. 3 shows the spectra corresponding to $CoAl_2O_4$-Asp-600°C and $CoAl_2O_4$-Asp-1100°C samples. In both cases, cobalt–oxygen-stretching modes are assigned in the frequency range of 450–700cm$^{-1}$ associated with the vibrations of Co–O, Al–O, and Co–O–Al bonds (Salavati-Niasari et al., 2009). In both FT-IR spectra is evident three distinct and sharp bands at 500, 560 and 667cm$_{-1}$ characteristic of the spinel $CoAl_2O_4$ in complete agreement with those observed in other reported studies (Salavati-Niasari et al., 2009-Li et al., 2003).

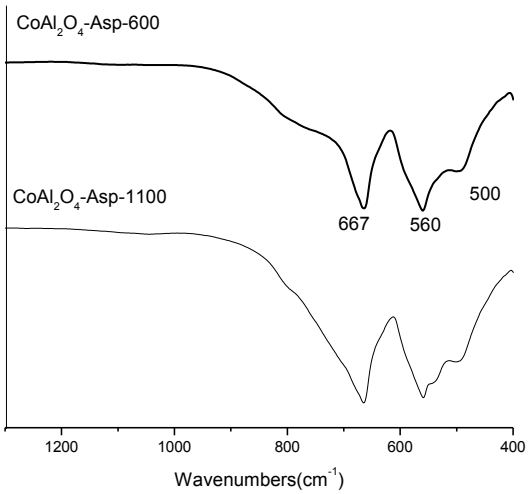


Fig. 3. FT-IR spectra of $CoAl_2O_4$-Asp-600° (up) and $CoAl_2O_4$-Asp-1100°C (down).

SEM micrographs of $CoAl_2O_4$-Asp-600°C, $CoAl_2O_4$-Asp-1100°C, $CoAl_2O_4$-Lis-600°C and $CoAl_2O_4$-Lis-1100°C are shown in Fig. 4 where the scale indicates 1μm. All of them present agglomeration as observed in $CoAl_2O_4$ powders obtained by hydrolysis of mixed metal alkoxides methods (Otero et al., 1999). In powders calcined at 600°C it is evidence more compact soft porous structures than in samples calcined at 1100°C, where additionally can be noticed submicrometric monocrystalline particles.

Fig. 5 shows TEM micrographs of $CoAl_2O_4$-Asp-600°C, $CoAl_2O_4$-Asp-1100°C, $CoAl_2O_4$-Lis-600°C and $CoAl_2O_4$-Lis-1100°C samples. The scale indicates 20 nm. In all them, it is observed a polyhedral form. Samples calcined at 600°C have an average particle size about 10 and 100nm, while both samples calcined at 1100°C are around 200 and 500nm. Then, a proportional increment in average particle size with the temperature was observed. This tendency has been observed in $CoAl_2O_4$ powders obtained by sol-gel process (Otero et al., 1999) where particles grown from 30 to 100nm.

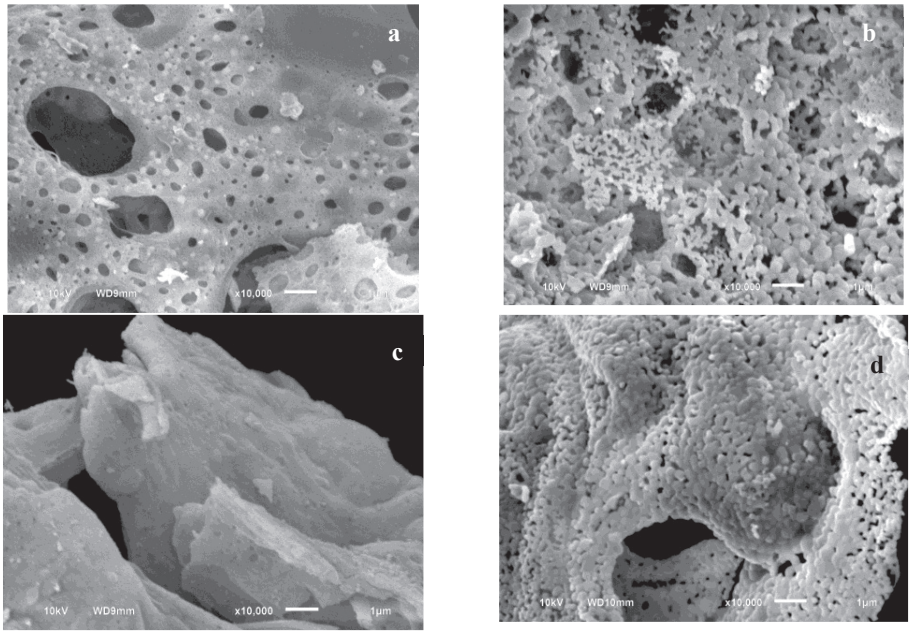


Fig. 4. SEM Micrographs of: a) $CoAl_2O_4$-Asp-600°C, b) $CoAl_2O_4$-Asp-1100°C, c) $CoAl_2O_4$-Lis-600°C and d) $CoAl_2O_4$-Lis-1100°C.

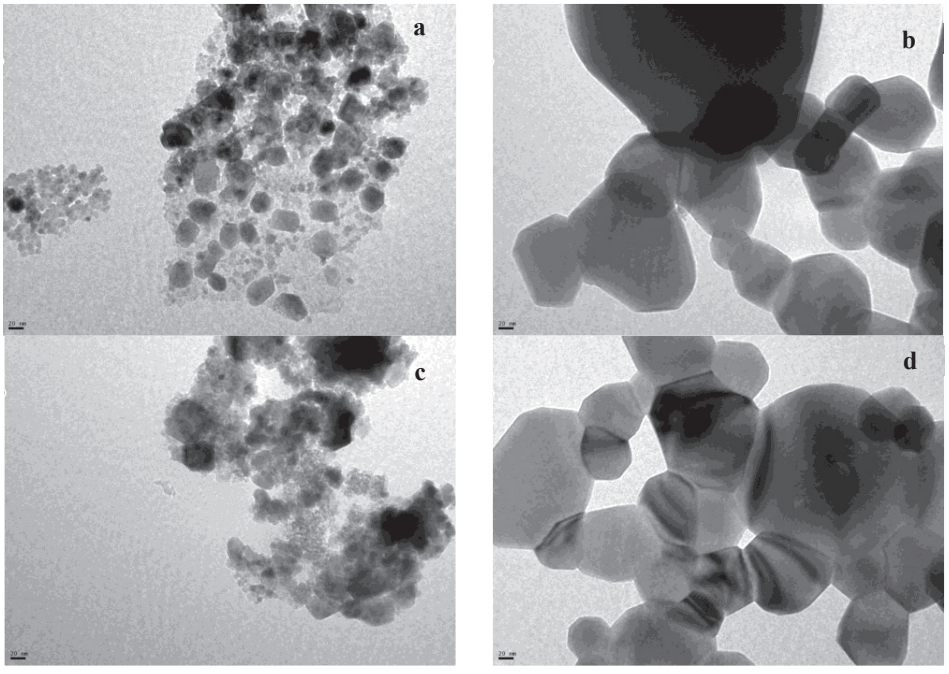


Fig 5. TEM Micrographs of: a) $CoAl_2O_4$-Asp-600°C, b) $CoAl_2O_4$-Asp-1100°C, c) $CoAl_2O_4$-Lis-600°C and d) $CoAl_2O_4$-Lis-1100°C.

## 4. Conclusion

$CoAl_2O_4$ samples were synthesized through combustion methods using aspartic acid (Asp) or lysine (Lys) as fuels. The powders obtained were calcined at temperatures between 600°C and 1100°C. All samples presented the spinel (*Fd-3m*), face centered cubic crystal structure of $CoAl_2O_4$. This structure was verified by FT-IR. The average crystallite size was around 24 and 200nm and it tended to rise by the effect of calcination temperature according to observation. It was observed in all samples a high degree of agglomeration of polyhedral particles in a range of 10-500nm, where the average particle size grown with the calcination temperature. In the light of these results it is suggested the use of even higher calcination temperatures so as to obtain opaque pigments for solar collectors selective paints.

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